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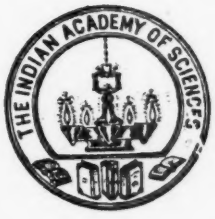

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THE STRUCTURE OF AMETHYST QUARTZ AND THE ORIGIN OF ITS PLEOCHROISM

By Sir C. V. Raman and A. Jayaraman
(*Memoir No. 58 from the Raman Research Institute, Bangalore*)

Received November 6, 1954

1. Introduction

By reason of the very beautiful colour which amethyst exhibits, this material has been used as a gem-stone since ancient times. Much interest therefore attaches to the problem of the origin of its colour, for a solution of which we need to know how amethyst and colourless quartz differ in respect of their structure. In the present investigation we have sought to elucidate the nature of this difference by a fact-finding study of those properties of amethyst which are calculated to throw light on its physico-chemical make-up. The results have led us to a view of the nature of amethyst which is altogether different from those which have found expression in the extensive literature of the subject, but which nevertheless appears to be both simple and natural.

2. The Density of Amethyst Quartz

If the colour of amethyst were due to the presence of appreciable quantities of the oxides of heavy metals such as manganese or iron, as has sometimes been suggested, we may expect this to come into evidence in precise determinations of the density of the material. For such a test, it is clearly necessary to use specimens which do not exhibit visible cracks, inclusions or surface impurities. We have therefore chosen to work with selected material in the form of cut and polished gem-stones. A Sartorius analytical balance was employed and the density of each specimen was measured in the usual manner by transferring it from a cup in air to a second cup held suspended by a fine wire under water. Table I shows the densities thus determined of six pieces of colourless quartz, while Table II shows the corresponding results obtained with thirteen different specimens of amethyst. Necessary corrections were made in each case for the temperature of the water and the buoyancy of air. The remarks made against each specimen in the Tables indicate its optical behaviour.

It will be evident from a comparison of the figures in the two tables that in the case of colourless quartz of the best quality, the density comes out consistently as 2·651, the uncertainty not exceeding one unit in the

TABLE I

Density Determinations with Quartz

Description	Mass in grams	Density in grams per c.c.	Remarks
Quartz crystal with natural faces	3·9264	2·651	Very transparent and free from inclusions
do.	0·595	2·650	do.
Polished quartz sphere I	4·7197	2·652	A few needles inside but quite transparent
Polished quartz sphere II	3·7886	2·651	Very transparent and free from inclusions
Polished quartz sphere III	2·5042	2·653	Exhibits a weak star due to inclusions
Polished quartz sphere IV	2·4194	2·667	Exhibits a markedly diminished transparency and a bright star due to inclusions

TABLE II

Density Determinations with Amethyst

Description	Mass in grams	Density in grams per c.c.	Remarks
Intensely coloured	2·3394	2·651	
do.	1·8521	2·652	
do.	1·3466	2·651	
do.	1·0846	2·652	
do.	0·7137	2·650	
Moderately coloured	2·2276	2·651	
do.	1·4184	2·650	
do.	1·2545	2·650	
Lightly coloured	3·1782	2·650	
do.	1·1595	2·653	
do.	1·1937	2·651	
do.	1·0351	2·650	
do.	0·7481	2·654	Visible inclusions

last decimal place. On the other hand, colourless quartz containing inclusions gives definitely higher values. The determinations for amethyst do indeed show variations in the third decimal place, but these deviations are in no way correlated with the depth of the colour exhibited by the specimen. The differences are therefore either purely experimental or else arise from residual defects in the specimens which are indeed noticeable when they are critically examined under immersion in a liquid cell.

The data appearing in the two tables give no support to any explanation of the origin of the colour of amethyst as due to metallic impurities. On the other hand, *they show quite definitely that the density of amethyst quartz does not differ measurably from that of colourless quartz of optical quality.*

3. The Scattering of Light in Amethyst

Colourless transparent quartz free from internal inclusions gives an observable scattering of a blue colour and of uniform intensity when traversed by a concentrated pencil of sunlight. But the effect is extremely weak and is observable only in favourable circumstances. Figure 1 in Plate X shows a transparent crystal of quartz of optical quality immersed in a cell containing carbon tetrachloride and traversed by a beam of sunlight. The track of the beam in the liquid appears in the photograph, but the track within the crystal is hardly to be seen by reason of its extreme weakness.

Figure 2 in the same Plate shows a similar experiment with a crystal of smoky quartz immersed in a cell containing distilled water. It will be noticed that the Tyndall track within the crystal is conspicuously observable.

Figure 3 in the same Plate is a photograph of a crystal of amethyst quartz immersed in carbon tetrachloride. The track of the beam in the liquid both before entry into the crystal and after emergence from it is very conspicuous. Within the crystal itself, there are two regions adjoining its rhombohedral faces in which no track is visible. These regions are precisely those which exhibit the amethystine colour, while the region midway between them exhibits a conspicuous Tyndall effect which is due to inclusions present in this colourless part of the quartz. The crystal had a density of 2·563, which is slightly higher than that of pure quartz, thus indicating the presence of such inclusions.

Figure 4 in the same Plate is a photograph of a cut gem of amethyst immersed in a cell containing carbon tetrachloride and traversed by a beam of sunlight. Here again, the track of the beam is totally invisible within the crystal.

Visual observations with all the specimens of amethyst listed in Table II yielded the same result. Hence we conclude as follows: *amethyst quartz does not exhibit the Tyndall scattering so conspicuously observable in the case of smoky quartz; its behaviour in this respect is comparable with that of colourless transparent quartz.*

4. X-RAY DIFFRACTION STUDIES

The experimental facts set forth in the two preceding sections appear very significant. It seems difficult to reconcile them with any explanation of the colour of amethyst as due to impurity material present in a colloidal or even in a molecularly dispersed form. Nor does it appear easy to reconcile them with an attribution of the colour to defects or imperfections of crystal structure or to a stoichiometric deficiency or excess of either silicon or oxygen in the lattice. On the other hand, they fit in perfectly with the hypothesis that amethyst is a crystalline material very similar to colourless quartz but with a different electronic configuration. Such configuration might well belong to a lower symmetry class than that of α-quartz, and this would immediately account for the fact that amethyst is optically biaxial whereas colourless quartz is uniaxial. A different electronic configuration belonging to a lower symmetry type would necessarily involve an alteration in the electronic energy levels and hence also to an altered absorption spectrum. The pleochroism and the optical characters of amethyst would thus both find a natural explanation on the present view of its structure.

It is evident from the foregoing that a thorough study of the pleochroism of amethyst and of its absorption spectra should prove useful in dealing with the problem of its structure. Such a study has been carried out at this Institute by Mr. S. Pancharatnam and his results are reported in the paper following the present one in the same issue of the *Proceedings*. We shall not traverse the same field here but will proceed to describe the results of an entirely different technique for investigating the problem under issue.

If colourless quartz and amethyst differ in their electronic configurations, comparative X-ray diffraction studies may be expected to reveal the existence of such differences and even to indicate their nature and magnitude. In view of the near resemblance between the two structures, it appeared unlikely that the usual methods of X-ray structure determination would prove useful in this connection. We have therefore chosen to adopt a different technique which we shall now proceed to describe and which is based upon certain well-known facts regarding amethystine quartz.

A section plate of amethyst cut in any arbitrary direction often exhibits a variety of features. Commonly noticeable is the appearance of bands of colour alternating with clear quartz running parallel to the intersection of a rhombohedral face of the crystal with the surface of the section plate. Sectors exhibiting different colours are also noticeable on section plates cut obliquely to the trigonal axis of quartz. Thus, if a pencil of X-rays traverses such a section plate, the material over different parts of the area should exhibit differences in the X-ray reflection intensities corresponding to the optically observable features on the plate. In this connection, however, some important remarks are necessary. As is well known, any mosaicity or imperfection in crystal structure would reveal itself in a general increase in the intensity of X-ray reflection. Hence, what we have to look for in the present case is not an enhancement of reflection intensity corresponding to the areas of colour on the plate, but differences in X-ray reflection intensity which vary with the particular crystal planes giving the reflections and hence connote real differences in crystal structure in the different areas on the plate.

It has also to be remarked that quartz often exhibits internal twinning. If such twinning be of the electrical type, areas on the plate in which the electric axis is oppositely orientated would, in general, give different X-ray reflection intensities. Hence it is essential to work with section plates in which electrical twinning is absent.

5. Technique and Results of Study

A plate about 1 millimetre thick and about 2 cm. by 1·5 cm. in area was cut out from a large clear crystal of amethyst. The plate exhibited both the bands and sectors of colour described earlier. By fine grinding the surfaces of the plate and then etching with dilute hydrofluoric acid and examining them under a spot-light, it was verified that the area on the plate chosen for the study and which exhibited the bands and sectors of colour was completely free from both optical and electrical twinning. The absence of optical twinning was also independently verified by an examination of the plate between crossed polaroids when immersed in a cell containing benzyl alcohol which has very nearly the same refractive index as quartz.

The X-radiation from a rotating target tube run at 50 mA and 60 kV emerged through a 1 millimetre hole and was allowed to diverge until the area of the crystal plate was completely bathed by the beam at a distance of about 40 cm. A photographic film was placed at a distance of about 10 cm. behind the crystal plate. This distance was found to be

sufficient to avoid overlapping of the Laue reflections which in these circumstances are necessarily of rather large size. In effect, each Laue spot recorded on the photographic film presents a picture of the irradiated area of the crystal.

Figure 1 in Plate IX is a reproduction of the larger part of a Laue diagram obtained in the manner described above. At the centre of the picture has been placed in its correct orientation a photograph taken by transmitted sodium light of the area of the crystal plate actually employed in X-ray diffraction. It will be seen that the plate exhibits a set of parallel bands towards the left, while at its centre and towards the right appear a pattern of sectors which by ordinary daylight exhibit the different colours indicative of their pleochroism. Fainter bands are also visible towards the upper right-hand corner.

On a scrutiny of the pictures of the crystal appearing in the figure as Laue reflections, the following features emerge. All the pictures exhibit varying degrees of distortion, but this does not prevent us from comparing them with the optical picture of the crystal appearing at the centre of the figure. The latter, it should be mentioned, has been slightly enlarged to make the comparisons easier. Two irregular bright streaks appear in all the pictures; these arise from defects in the crystal which were readily visible on a direct examination and are irrelevant for our present purpose. Some of the stronger Laue reflections exhibiting significant features have been numbered as a series from 1 to 9 for convenience of reference. Number 1 shows prominently the set of parallel bands appearing on the left of the crystal plate. The same bands can be seen faintly in some others of the numbered spots but are invisible in No. 6. The large sector appearing at the centre of the plate presents very different aspects in the different spots. Compare, for example, Nos. 2, 3, 6, 8 and 9. The complex pattern of sectors on the lower right of the specimen can be made out in several of the pictures but presents altogether different aspects in them. Compare for example, Nos. 3 and 8. The bands seen in the upper right-hand corner of the crystal are very conspicuous in Nos. 2 and 3 but are weak in Nos. 6 and 9. The record thus clearly establishes that amethyst is a crystalline solid which gives coherent X-ray reflections, the intensities of which differ from those of colourless quartz and are also different for areas exhibiting different colours by transmitted light. A correlation is thus established between the pleochroism of amethyst on one hand and its crystal structure on the other hand.

FIG. 1. Laue Pattern of Amethyst Section Plate

FIG. 1 FIG. 3

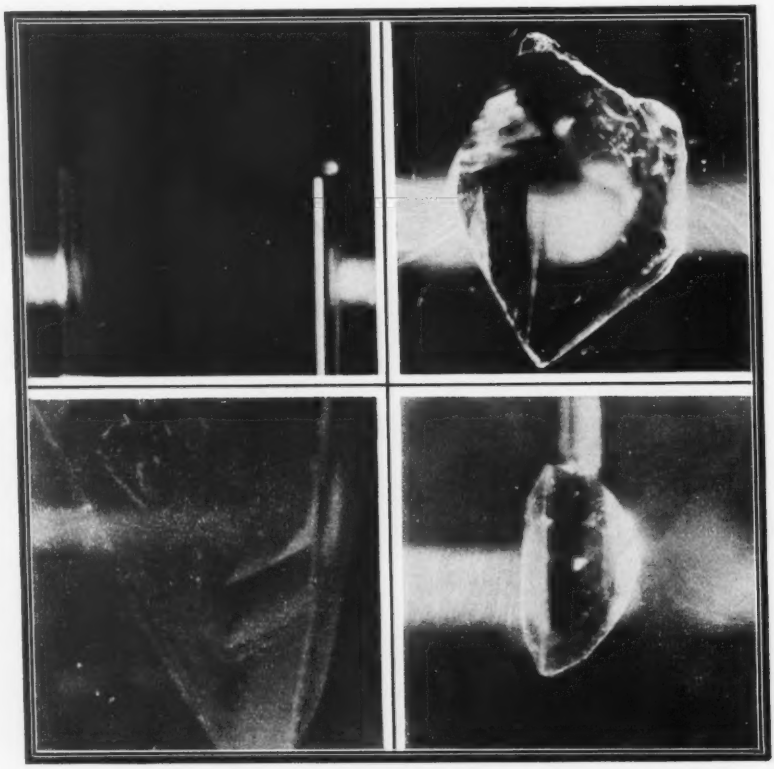

FIG. 2 FIG. 4

Scattering of Light in Clear Quartz, Amethyst and Smoky Quartz

6. Acknowledgement

We wish to take the opportunity of expressing our gratitude to Sir Purshotamdas Thakurdas for his generous gift of the rotating-target X-ray set manufactured by Messrs. Newton-Victor which has been used in the present investigation.

7. Summary

Comparative measurements with clear quartz and amethyst show conclusively that these two materials do not differ measurably in their density. Amethyst and clear quartz also resemble each other in not giving any Tyndall effect of the kind so conspicuously observable with smoky quartz. These facts indicate that amethyst is a crystalline material very similar to colourless quartz in its make-up, but with a different electronic configuration belonging to a lower symmetry class. The optical biaxiality and the pleochroism of amethyst then follow as natural consequences. This view of the nature of amethyst is confirmed by X-ray diffraction studies made with a section plate of amethyst free from internal twinning but exhibiting colour bands and colour sectors over its area.

ON THE PLEOCHROISM OF AMETHYST QUARTZ AND ITS ABSORPTION SPECTRA

By S. Pancharatnam

(*Memoir No. 59 from the Raman Research Institute, Bangalore*)

Received November 10, 1954

(Communicated by Sir C. V. Raman)

1. Introduction

It is well known that the purple variety of quartz, amethyst, is pleochroic: in other words, one of the factors on which its spectral absorption depends is the direction that the vibration in the crystal makes with reference to the crystallographic axes of quartz, *viz.*, the *c*-axis, and the three electrical *a*-axes. On the precise nature of this dependence however, existing data[1-4] appeared to us inadequate—and hence this investigation. The usefulness of such a factual study will be apparent; for any detailed theory of the mechanism of the absorption which gives to amethyst its purple colour, must, of necessity, also explain the observed features of the pleochroism.

2. General Features

A complete analysis of the pleochroism of amethyst, it might be thought, requires merely a study of the absorption for the vibration-direction along the optic axis, and for one normal to it (regarding the material as non-rotating along directions oblique to the *c*-axis). That the matter is not so simple however, would appear at once on examining an arbitrarily cut section of amethyst.

A characteristic feature of the typical amethyst section-plate, and one that has evoked attention, is the manner of distribution of the colour. The colour is not spread uniformly over the area of the plate but segregated into a number of discrete geometric *sectors*. Examination of an arbitrarily cut section through a polaroid reveals a pleochroism that is truly remarkable; remarkable firstly for the very pronounced contrast not only in the intensity but also in the hue of the colours shown by any one sector, for the two vibration-directions; and secondly in that the pleochroism of the different sectors are entirely dissimilar, though, in general, uniform over any one sector.

With each well-defined segment of colour it is usually possible to associate a rhombohedral face of the main crystal, since such sectors

generally show certain well-known characteristics of which excellent illustrations may be found elsewhere.[5-7] Among such characteristics are: proximity of a coloured segment to a natural rhombohedral face, or to a similar 'artificial face' formed by an impurity-plane running within the crystal; the occurrence of triangular or horn-shaped sectors with apices pointing inwards, and bases spanning or turned towards the corresponding rhombohedral faces; the presence, within a sector, of laminations, or of lighter and darker layers of colour, with the plane of the banding appearing parallel to a pair of parallel rhombohedral faces—the face in question being located uniquely by the criterion of proximity, or from an inspection of the grouping of sectors. It would appear then, natural to ask whether any relation connects the pleochroism of a uniformly behaving sector with its associated rhombohedral face.

In describing certain of the pleochroic features shown by an arbitrary section of amethyst, we have refrained from mentioning certain further complications that occur not infrequently; namely the presence even within a sector, of discrete patches of colour showing entirely different pleochroic behaviour, as also of areas of colour with a non-descript, non-uniform pleochroism. The fact is that the pleochroism is dependent not only on the segmental colouration but also on yet another characteristic feature of most amethyst plates, namely, twinning—to a discussion of which we now turn.

The theory that the amethystine colour is in some manner due to the close twinning of the enantiomorphous forms of quartz,[8] had at one time obviously such currency, that 'amethyst' came as much to signify optically twinned quartz, as to denote that purple variety that goes by that name today. Nevertheless Brewster,[9] and later Brauns,[10] reported that the colour was not due to optical twinning—though the latter had at one time held views to the contrary[6,11]; and our observations, to be described later, completely substantiate their conclusions—it being possible to obtain areas of colour with no detectable traces of twinning.

To say that twinning is not the cause of the colour is not to say that it does not affect the colour in any manner whatsoever. For, where twinning—of either the optical or electrical variety—intrudes into, or subdivides a coloured region, the colour and pleochroism at the region of intrusion are observed to be clearly modified. (A case of this sort has, for example, been mentioned by Groth[5].) And this factor must obviously be taken into account in studying the pleochroism.

Broad recognition had been taken, not only of all the general features till now outlined, but of some more. Of these a particularly important

property, and one that becomes quite pronounced for the more densely coloured regions, is the invariably present biaxiality of uniformly behaving sectors—a feature which, it has been reported,[12] can be driven away together with the colour by heat. It is in the pleochroism, however, more than in the refractive properties, that the fall from uniaxial symmetry is most complete: for there is in it no general tendency towards diminution, much less towards complete disappearance, as the *c*-axis is approached.[1-3]

3. PRELIMINARY STUDY OF THE MATERIAL

For reasons already indicated, it was necessary, prior to the study of the pleochroism, first to select untwinned areas of colour in which the material of different sectorial species did not overlap, and which could be associated with corresponding rhombohedral faces; secondly to determine the handedness and where possible, the orientation of the positive directions of the *a*-axes in such areas: that the pleochroism depends on these factors being inferred from the complications caused by the incidence of twinning. This section contains merely the particulars of such a preliminary study; and we have thought it fit to describe this study in some detail because of its relevance not only to the topic of the pleochroism, but also to the twinning theory of the origin of the colour mentioned previously.

Those specimens which were in the form of plates were given a weak etch with dilute hydrofluoric acid, preceded by fine grinding of the two surfaces and followed by examination of the gross reflection sheen under a spot-light; the areas of the surface occupied by separate twin members could, in this way, be thrown into relief, and the actual twin-boundaries—both optical and electrical—easily located. While both sectorial as well as extremely patchy twinning patterns are common, the etch technique, in conjunction with optical tests to be described, showed that coloured areas with no detectable traces of twinning occur quite frequently. Most strikingly and impressively indicating that twinning was not a necessary accompaniment of colour—or even of the banding of colour—were two flawless specimens, both nearly a square inch in area, cut from the same crystal, having several discrete coloured segments and with the major area of the plate made up of one untwinned entity.

For roughly basal sections, the positive directions of the *a*-axis in any required sector, was determined by the etch technique—the entire procedure followed being that found described in detail elsewhere.[13] This together with a knowledge of the handedness of the sector yielded by optical study (though indeed, the etch method is capable of giving even *that* information for basal sections) enabled us to find whether the rhombohedral face

associated with any particular sector belonged to the primary or the secondary rhombohedron. The result emerged that sectors of both 'primary' and 'secondary' types do occur. We shall find it convenient to refer only to the handedness and 'type' (*i.e.*, primary or secondary) of any sector, omitting mention of the polarity of the *a*-axes, since this, in any case, is got from a knowledge of the first two features. In amethyst material from Hyderabad, from which many of the specimens were taken, it is possible that primary sectors are a rarity, except as lightly coloured zones separating more dense secondary sectors.

Arising from the contrary rotation of the enantiomorphous forms, optical twinning and its disposition in the depth of the material could be studied by the usual optical procedure of examination in white and monochromatic light; for this, the specimen, immersed when not a basal plate, was viewed between polaroids, precisely along the central direction of the optic figure as seen in the *uncoloured* areas. Attention has previously been called to the presence of pleochroism along the *c*-axis, and to the biaxiality of every amethystine sector: in the optical examination, these two conspire to give a somewhat misleading appearance, which can in practice, when the colouration is not intense, be distinguished from the effect due to a colour-boundary being a true twin-boundary. (We may mention, in passing, that the manner in which the twinning boundary, in certain cases, closely follows the colour-boundary is something remarkable.) Mapping of the twinning in contiguous uncoloured areas was in many cases generally useful, *e.g.*, for showing where any twinning shoots from the uncoloured regions might possibly pierce the segment; and where twinning at the colour boundary was absent, such examination was most convenient for determining the handedness of the segment—since the determination of the sign of rotation for uncoloured areas poses no problem.

In the convergent-light figure through an optically untwinned sector, Airy's spirals—formed when right and left material overlap—should be conspicuously absent. The isolation of the convergent light through even a small sector, which is of the essence in such tests, could be done with the aid of a single pocket lens—the eye being kept in a position conjugate to the sector. In an untwinned sector the black isogyres seen with crossed polaroids should not penetrate, as such, into the slightly distorted uniaxial figure shown in light or moderately coloured areas; while when the more biaxial regions were under test, it was similarly verified that by setting one polaroid parallel and the other perpendicular to the axial plane, the isogyre lying in this plane did not pass unmodified through the eyes. The

handedness of the sector (adopting the observer's standpoint) is the same as the sense in which the analyser should be rotated for the rings to expand in the former case, and for the eyes to be extinguished in the latter. For thin sections the direct method of determining the handedness of coloured regions will be stated later—the above methods not being feasible.

Certain rare cases occurred where sectors satisfied the tests for twinning described above, and yet did not show absolutely uniform characteristics; these we interpret as due to the difficulty of detecting small traces of twinning—especially of the electrical variety—in the depth of the material, and to the possibility of the overlap of the material of different sectorial types. In any case, uniformity of pleochroism was itself included among the criteria of selection; and we now proceed to give the substance of our observations on coloured areas satisfying these criteria.

4. EXAMINATION OF THE PLEOCHROISM IN PARALLEL POLARISED LIGHT

(*a*) *Absence of uniaxial symmetry*

To avoid any effects connected with the presence of optical activity[1-3] and heterogeneity of the coloured material in the depth of the specimen (Johannsen[14]), it was thought advisable, in the first instance, to investigate the pleochroism at oblique directions to the *c*-axis. Viewed thus, moderately coloured and uncoloured areas showed the same extinction positions between crossed polaroids—the entire material being regarded for our qualitative purposes, as non-rotating along such directions. In consequence the absorption for the various directions of vibration in the optical indicatrix, could be conveniently scanned in the following fashion. (And it is to be implicitly understood that throughout this section all description of pleochroic behaviour refer to observations made with the arrangement to be now described—with the specimen to be examined kept all the while in an immersion fluid.)

Against the background of an extended source of white light a polaroid was set, with its vibration-direction vertical. The direction of sight was kept horizontal. By mounting the crystal—on a suitable contraption—with its *c*-axis always in the plane defined by these two directions, the vibration of the incident light lay automatically always on a principal plane. The optic axis could first be set at any desired inclination to the vertical by tilting the specimen about a horizontal axis perpendicular to the line of sight; the specimen could then be taken through a complete revolution about its own *c*-axis—a suitable arrangement being made for performing these two operations.

Any provision for the last operation—which shows the absorption as the vibration is taken over a cone of directions described about the *c*-axis—would be superfluous for an absorbing system having uniaxial symmetry. This however is what amethystine sectors do not possess. Not only does the colour of any one sector not remain constant as the specimen is so rotated; a rotation of 180° may in general leave the colour profoundly altered, showing that the *c*-axis cannot even be a diad axis of symmetry as far as the pleochroism is concerned. To stress these points we refer briefly even at this stage to Figs. 1 and 2 in Plate XI, which show the respective wedge-type spectrograms for two vibrations both inclined at 45° to the optic axis of the quartz and both lying in a plane containing this axis. The large difference in the colour of the sector for these two polarizations (Fig. 1—deep red; Fig. 2—clear blue) is reflected in their dissimilar absorption spectra.

(*b*) *A relationship between sectors*

It would next be necessary to see whether any relation holds between the pleochroism of different sectors, before observations on a single sector can have much significance. The loss of trigonal symmetry suggests that the different observed species of pleochroism perhaps correspond to different possible orientations (with respect to the crystallographic features of quartz) of the same non-uniaxial absorbing system.

Those plates having two or three sectors of the same handedness, but associated with adjacent faces of either the primary or the secondary rhombohedron, were examined in polarized light in the arrangement described above. Independent of the tilt of the *c*-axis, it was found that on rotating the specimen about this axis, such adjacent sectors went through the same cycle of colours, but with a 'lag' of 120°—which caused them to appear differently coloured at any one setting. The angle was arrived at in the case of specimens with two such sectors by noting the position at which each sector went through a particularly notable colour change in the cycle; and more accurately for the triple-sector plates by noting the successive azimuths at which the different pairs of adjacent sectors (selected in cyclic permutation) showed a matching of the hues within the pair. The point to note is that the pleochroism of sectors of similar handedness and type (*i.e.*, primary or secondary) bear the same relation to their reference rhombohedral faces. For the vibration along the optic axis the sectors, as may be expected, are identically coloured. This is also the case when the specimen is viewed along the optic axis in unpolarized light.

(*c*) *Existence of a symmetry axis*

The existence of any element of symmetry for the absorption characteristics of a single sector cannot *a priori* be assumed; but if a symmetry axis does exist then any two vibration-directions in the (roughly uniaxial) optical indicatrix which are related by a rotation of 180° about this axis are equivalent as far as the absorption in that sector is concerned. Detection of such equivalence, involving as it does the comparison of the colour of a sector for two entirely different orientations of the specimen, would be difficult if attempted directly. But the absorbing system is effectively present in several different orientations on the same plate—in the form of several sectors; so that we may be led to significant conclusions if we attempt to find the loci of vibrations for which two sectors are identically coloured.

When comparing the pleochroism of adjacent sectors of similar handedness and type, by the method described, we referred to the equality in the colour-tone attained by any two such adjacent sectors at certain azimuths during the rotation: these occurred at positions 180° apart. Set at one such azimuth, a tilting of the specimen about the horizontal axis normal to the line of sight, or the turning of the polarizer to a perpendicular position, altered the hue of the two sectors together without destroying their match. In other words: for the vibration normal to a particular plane A containing the optic axis, as also for any vibration lying in this plane, the two sectors are identically coloured. (To fix our ideas, we may remark that the plane A turns out to be normal to one particular *a*-axis of quartz.) Remembering that the second sector is simply in that position which the first would occupy when rotated by 120° in, say, a clockwise sense, it should be possible to transform the above statement to one involving the first sector alone. So let us draw a plane B, got by rotating A in the opposite sense (anticlockwise) by 120°, about the *c*-axis. Then we can say: the two vibrations normal to A and B, as also any two vibrations which lie respectively on A and B and are related by a 120° rotation about the *c*-axis, are equivalent as far as the absorption in the first sector is concerned. If—though the above statement is only qualitative—we regard this equivalence as the expression of a symmetry element possessed by that sector, we may derive a further conclusion; for, any two vibrations of the type described are related to one another only by the following possible operations: (*a*) reflection across a plane C bisecting the obtuse angle between A and B; (*b*) a rotation by 180° about the normal to such a plane; (*c*) a rotation of 120° about the optic axis. And since the pleochroism is not in conformity with trigonal symmetry, the absorbing system in the sector has, qualitatively speaking,

a plane of symmetry C, or a digonal axis of symmetry normal to such a plane, or both. (It is not possible to distinguish between these cases, insofar as we consider, for our qualitative purposes, that the two waves propagated without change of form in any direction oblique to the *c*-axis, are plane-polarized and thus have no handedness or sense.)

The symmetry axis of the sector (as we shall henceforth call the normal to the plane C) was found qualitatively to coincide with one of the crystallographic *a*-axes of quartz: and this *a*-axis passed through one corner of the rhombohedral face associated with the sector. (These conclusions followed from the fact that the plane A—whose azimuth could be placed to within 15°—was normal to a rhombohedral face associated with one of the two adjacent sectors concerned.)

The existence of the symmetry axis for the pleochroism of any sector received confirmation in the following manner. Two basal plates each with one large sector were mounted side by side, in the first instance with their triangular sectors in parallel orientation and with their *c*-axes in line, in such a fashion that the two sectors were checked to show the same pleochroism at all tilts (confined to oblique directions to the *c*-axis). One of them was then turned over by rotating it through 180° about the axis expected to be the symmetry axis of the sector concerned. The two sectors still showed identical pleochroism at all orientations.

5. The 'Trichroic Colours' and Their Absorption Spectra

We have seen that one axis of the absorption-ellipsoid for any wavelength in the visible coincides with, or at least does not disperse far from, an *a*-axis of quartz passing through a corner of the rhombohedral face associated with the sector. The absorption for vibrations on a plane perpendicular to this—on which the other two axes of the ellipsoid are constrained to disperse—could be examined in the following way: keeping the plane of the incident vibration horizontal, the sector could be tilted about its symmetry axis, after setting this vertical and normal to the line of sight. It was then found that two vibrations on this plane both inclined at 45° to the *c*-axis (β and γ in Fig. 1) represented the rough regions of two extremal positions of the colour intensity. For one of these vibrations the absorption was most intense, and the colour in artificial illumination, a very deep red (with perhaps a tinge of purple)—the corresponding wedge-type spectrogram, illustrated in Fig. 1 in Plate XI, showing an absorption maximum in the neighbourhood of 5250 Å. For the other vibration the colour was blue and the absorption maximum, as may be seen from Fig. 2 in Plate XI, was near 5750 Å. Fig. 3 in the same Plate (obtained at the

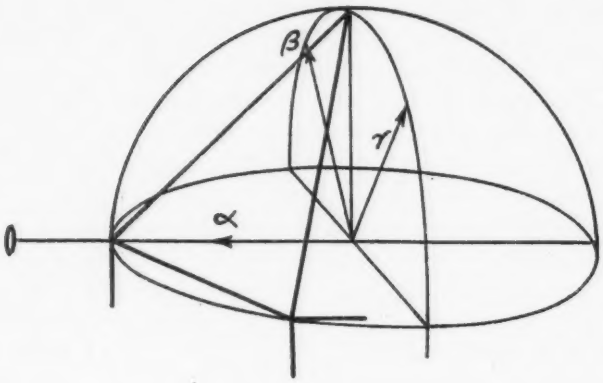

FIG. 1

latter tilt by turning the polarizer to a perpendicular position) gives the absorption spectrogram for the vibration along the symmetry axis a, for which the colour was a light orange. This represents the least absorbed vibration-direction (especially to the eye, transmitting, as it does, the yellow-green wave-lengths of high visual luminosity), the absorption maximum occurring in the region of 5000 Å. For this last case, the apparent position and intensity of the absorption are perhaps slightly modified by the dip in that region of the spectral sensitivity of the photographic plates used (Ilford HP. 3). This may be seen from Fig. 4 in Plate XI which gives the direct spectrogram taken with the tungsten lamp illuminant and the glass optics used.

We should not be taken as implying that two directions both inclined exactly at 45° to the c-axis and in a plane normal to the symmetry axis a, are true axes of the absorption ellipsoid for all wave-lengths in the visible. If they were so, there would be (for practical purposes) no pleochroism in evidence when viewed along the diad axis of symmetry; the pleochroism, however, did not appear to be absent in this direction when a rough test was made.

Regarding the absorption spectrograms—which were taken by giving successive strips along the length of the slit, exposures increasing by a constant multiplying factor of 2·25—we may mention a few relevant experimental points. A Foucault's prism was used for polarizing the light. The specimen was immersed in water, and a rough allowance for refraction was made when tilting the plate. The section used being, roughly speaking, basal, the depth of the material traversed for the tilt corresponding to

Fig. 1 was only slightly larger than that for the tilt corresponding to Figs. 2 and 3 in Plate XI; the region of the very intensely coloured secondary sector that was used, was of larger area than the incident pencil of light; also the processing conditions in all three cases were roughly the same. These conditions being so, the fact that the exposures for the strips in Fig. 1 were 30 times (roughly), those for the corresponding strips in Figs. 2 and 3, serves to further emphasize the relatively great intensity of the band for the deep red ' axis of absorption '.

6. Observations in Convergent Light

Very intensely coloured untwinned sectors when viewed in unpolarized light roughly along the *c*-axis and tilted about in various directions, display such violent and rapid changes in the depth and hue of the colour, that the use of convergent light for studying the associated phenomena is immediately suggested. When this is done, an idiocyclophanous figure stands revealed.

In an optically inactive biaxial medium the reason why an idiophanous figure can be seen in the neighbourhood of an optic axis, if the pleochroism there is very pronounced, is well known. Roughly we may say, that for any direction the incident unpolarized light is split into two linear vibrations (as determined by the refractive index ellipsoid) the respective absorptions of which are determined by their intercepts on an absorption ellipsoid; in the neighbourhood of an optic axis, a small change in the direction of propagation, by causing an appreciable change in the inclinations of the two principal planes to the axial plane, will in general lead to a large variation in the total absorption—thus enabling an idiophanous figure to be seen. This generally takes the form of a dark brush interrupted by a bright spot in its passage through the optic axis. Further if the section of the absorption ellipsoid normal to that optic axis, has its principal diameters lying in and perpendicular to the axial plane, the dark brush occurs in the same position as would the isogyre of the biaxial interference figure when seen in ' the 45° position '.

The idiophanous figure in amethyst is illustrated in Fig. 5 in Plate XII. Diverging from the neighbourhood of the *c*-axis are four dark purplish brushes set against the lighter background of an orange coloured cross. By viewing in parallel light along the directions corresponding to these brushes, it is seen that in reality two of the brushes on one side of the thinner arm of the orange cross are of a somewhat reddish-purple colour, the other two being more bluish-purple. The entire figure is therefore in conformity with the existence of an axis of symmetry lying parallel to

the thinner arm of the cross, which is also found to be roughly coincident with an *a*-axis passing through a corner of the associated rhombohedral face—thus illustrating our previous findings in a simple manner. Similarly on moving over to an adjacent sector, the figure is rotated round by 120° (it being understood that the sectors are of the same handedness and type and are associated with alternating faces of the hexagonal pyramid).

Viewed between polaroids, such dense sectors are seen to be pronouncedly biaxial (Fig. 6 in Plate XII). The *c*-axis is, qualitatively speaking, the acute bisectrix, and the axial plane is found to contain the symmetry axis of the sector. The isogyres in the 45° position correspond roughly to the brushes seen in unpolarized light. The idiophanous figure, therefore, consists in reality of two hyperbolic brushes each interrupted in its passage through a corresponding optic axis—thus giving the intervening space the appearance of a cross in which one arm is thinner than the other.

The broad features of the phenomena observed in the vicinity of an optic axis of an optically inactive pleochroic medium can be fairly well explained even on neglecting the ellipticity of the two waves propagated without change of form in such directions (*vide* Pockels,[15] Drude[16]). We find empirically that the main features of the idiophanous figure in amethyst can be accounted for, on neglecting, also, the presence of optical rotation. Thus for any direction along the lightly coloured cross, though the vibration normal to the diad axis of symmetry is very strongly absorbed, the other half of the incident light emerges without much attenuation, and is coloured orange and polarized with its vibration roughly parallel to the diad axis. While, the large total absorption for directions along the brushes is because here *both* vibrations (being inclined at roughly 45° to the symmetry axis) have moderately strong and roughly equal absorption coefficients—intermediate between that for the symmetry axis, and for a vibration normal to it and the *c*-axis.

On inserting a polaroid with its vibration-direction perpendicular to the axial plane, the orange interspaces are practically suppressed, and replaced by a very deep purple cross set against a somewhat lighter purple background—which is exactly what should be expected. (It is in fact this purple cross which gives the appearance of being black isogyres in Fig. 6 in Plate XII, though this was taken with parallel polaroids.) Following one arm of the purple cross either way in the plane normal to the diad axis of symmetry, one is led to the blue and deep red ' axes of absorption ' mentioned in the previous section. On the other hand, when the polarizer is in the perpendicular position, the idiophanous figure is broadly unaltered,

but with the contrast very considerably increased, since no longer is half the incident light almost completely suppressed for the directions along the arms of the lightly coloured cross.

Such observations with a single polaroid afforded a ready and convenient means of locating the axis of symmetry for sectors with moderate and uniform colouration—for which insufficient depth of absorption prevented the idiophanous figure from being directly seen. The features observed were essentially the same, though present in a less contrasted scale, as those described in the previous paragraph. The two orientations of the polaroid for which the resultant figure produced was *symmetrical* with respect to its vibration-axis gave the symmetry axis of the sector, and the direction normal to it and the *c*-axis. In such tests, uniformity of the colouration along the depth of the material was apparently of the essence. For in many lightly coloured areas it was common to find optic interference figures showing up with a single polaroid, apparently because the medium there could not be regarded as constituting a single optical phase. But even in such regions the pleochroism at directions oblique to the axis became a constant and characteristic property.

Viewed between crossed polaroids set along and perpendicular to the diad axis, the slightly distorted uniaxial figure in light and moderately coloured areas, appeared symmetric with respect to these directions. (When the section was thin the cross at the centre was not absent—only nebulous; the sense of rotation when required was opposite to that in which the analyser should be turned from this crossed position, for the cross to open out into four spots.)

The fact that both the pleochroism and the biaxiality had, qualitatively speaking, a common axis of symmetry suggested that the presence of birefringence along the *c*-axis could be traced to the presence of pleochroism along the same direction. The contribution of the pleochroism in the visible to birefringence could be detected in certain oblique sections. A plate which roughly contained the symmetry axis of a particular sector as well as its deep red 'axis of absorption', illustrated this fairly well. The section was kept in front of the slit of a spectrograph between two polaroids both inclined at 45° to the principal planes, such that the upper half of the spectrum in Fig. 7 in Plate XII was illuminated through the moderately coloured sector, and the lower half through the contiguous uncoloured quartz. The interference bands channelling the spectrum, indicate as may be expected, a slight increase of the positive birefringence on the longer wave-length side of the absorbing regions, and a decrease

at shorter wave-lengths. For this particular orientation at any rate, no change from the birefringence of quartz, other than that due to the band in the visible can be seen. Nevertheless the biaxial interference figure did not give any definite indication of crossed axial plane dispersion; for when the figure in one particular sector was examined successively through an orange and a blue filter, the biaxiality was seen to be pronounced in the former case, but relatively feeble in the latter—which is more indicative of a progressive diminution of the axial angle towards shorter wave-lengths. *Apropos* of this, we may remark that, on comparing the spectrograms reproduced as Figs. 2 and 3 in Plate XI, a distinct indication of pleochroism in the ultra-violet band is in evidence.

7. Factors Fixing the Pleochroic Orientation

We may recall that the dependence of the pleochroism on two features—namely the handedness and 'type'—of any sector, has as yet not been clarified. When this is done, it is found that our qualitative picture of the pleochroism of any sector is completely fixed in terms of the associated rhombohedral face.

Looking from above the apex of the quartz pyramid, the symmetry axis of any sector was found to pass through the left or anti-clockwise corner of the associated rhombohedral face, when the sector was left-rotating; and *vice versa*. So that Fig. 1 is drawn correctly only if the sector happens to be right-rotating. This relation was found to hold for both primary and secondary sectors.

Again, the deep red position of the vibration was more oblique to the normal of the associated face than the blue, in the case of the primary sector; and *vice versa*, for a secondary sector. So that in Fig. 1 in the text, it is the vibrations in the vicinity of γ (and not of β) that are deep red if the associated face belongs to the secondary rhombohedron. If, therefore, the rhombohedral faces associated respectively with a primary and a secondary sector, both of the same handedness, are kept in parallel orientation, the two absorbing systems would be related to one another by a rotation of 180° about the *c*-axis.

8. The Relationship between the Pleochroism of Different Sectors

Arising from the dependence of the pleochroism on twinning and the sectorial property, various possible relationships between the pleochroism of different sectors on the same plate may be envisaged, and were in fact

met with. Three of these, the explanations of which may be got from a little consideration of our findings in the previous section, may be mentioned.

A right- and a left-rotating sector associated respectively with two adjacent faces of either the primary or the secondary rhombohedron, will have their symmetry axes either in line or inclined at 60°, depending on their mutual orientation. In a case of the former type, the pleochroism of both sectors were found to be identical at all tilts (confined to oblique inclinations to the *c*-axis). This was also true for a case where two sectors of complementary type had occurred on the same plate—by itself, a rare feature—the two being of the same handedness but associated with diametrically opposite faces of the hexagonal pyramid. In the third instance to be mentioned, a Dauphiné twin-boundary had cleft a coloured area in two; the two halves, though of the same handedness, were naturally of complementary types, so that their pleochroism were different; but, for all tilts it was only the colour for the 'extraordinary vibration' that differed, that for the vibration normal to the *c*-axis being identical in both the regions. These three cases involving as they do, a judging of the identity of two colour tones, lend support to our general interpretation of the remarkable pleochroism of amethyst quartz.

In concluding, the author wishes to record his deep sense of indebtedness to Prof. Sir C. V. Raman, for constant guidance and encouragement throughout the course of this investigation.

9. Summary

Amethyst is optically biaxial, and does not conform to the trigonal symmetry of colourless quartz, though the *c*-axis appears as the acute bisectrix in its biaxial figure. The pleochroic and biaxial properties taken together conform only to a symmetry of the monoclinic class, the axis of symmetry being coincident with one of the electrical axes of the colourless quartz in which it appears. For vibrations along this axis, the colour of the transmitted light is light orange (absorption maximum near 5000 Å); while for the two vibrations in the perpendicular plane which make approximately 45° on either side with the *c*-axis, the colours are respectively, blue (absorption maximum near 5750 Å), and a deep reddish-purple (absorption maximum near 5250 Å).

Which of the *a*-axes of quartz is the symmetry axis of amethyst is determined—in relation to the particular rhombohedral face with which the colour-sector is associated—by the right- or left-handedness of the segment; while the disposition of the other two colour axes with reference to the

associated face depends on whether this belongs to the primary or the secondary rhombohedron. Hence, the presence of any twinning naturally complicates the pleochroism.

Photographs are reproduced illustrating (*a*) the absorption spectra for the trichroic colours; (*b*) the idiophanous and biaxial figures seen through dense sectors in convergent light (the optic axial plane containing the symmetry axis); and (*c*) the anomalous dispersion of the birefringence.

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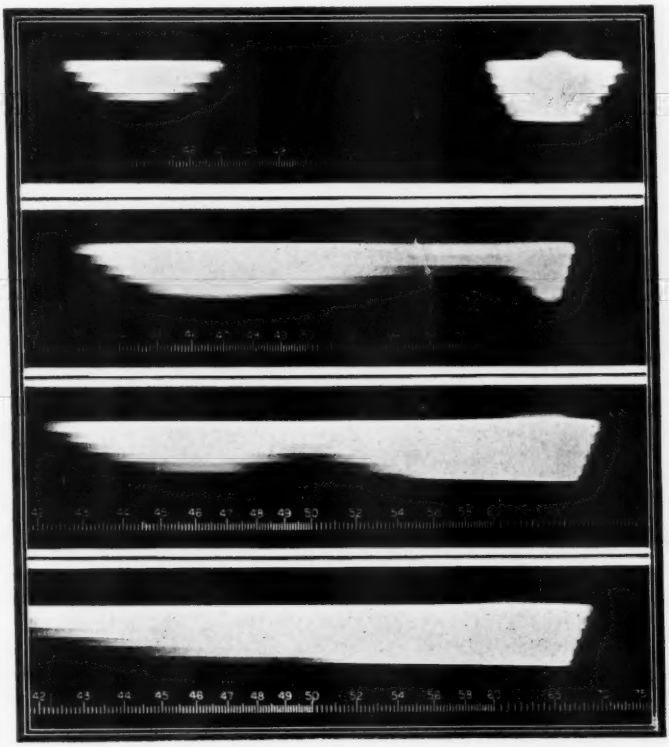

Absorption Spectra of Amethyst

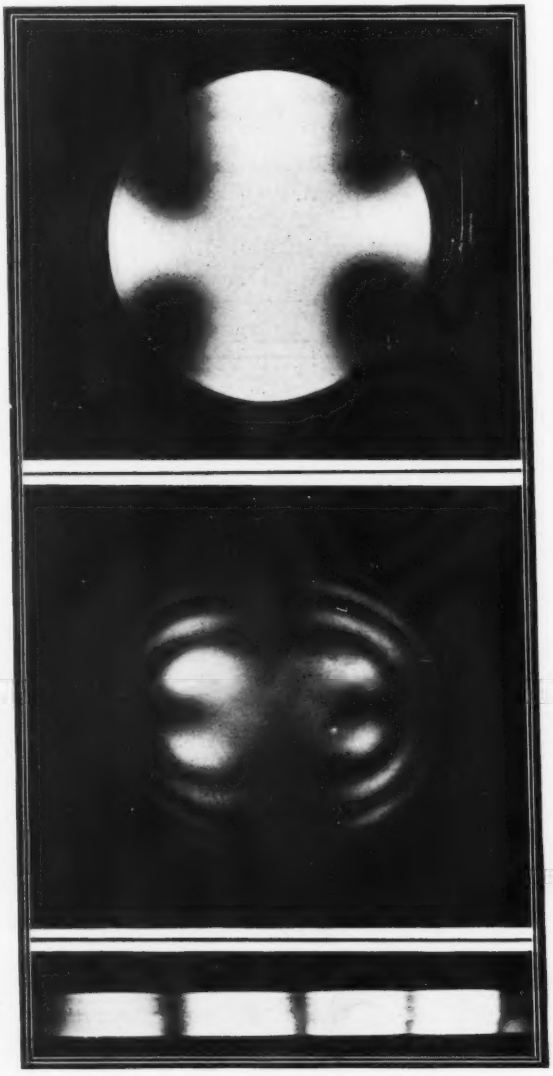

FIG. 5 Idiophanous Figure

FIG. 6 Biaxial Figure

FIG. 7 Anomalous Dispersion

Optical Behaviour of Amethyst

THE RAMAN SPECTRUM OF DIAMOND

By D. Krishnamurti

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1. Introduction

The Raman spectrum of diamond was first studied by Ramaswamy (1930) who noticed that it exhibits a single sharp and intense line with a frequency shift of 1332 cm.$^{-1}$ Bhagavantam (1930) who examined a number of diamonds reported $1331{\cdot}9 \pm 0{\cdot}3$ as the averaged value of the frequency shift. Subsequently Robertson, Fox and Martin (1934), who examined four diamonds which exhibited the 8μ infra-red absorption and five others which did not, gave $1332{\cdot}2$ cm.$^{-1}$ at 20° C. as the frequency shift. Nayar (1941) who undertook the study of a number of diamonds and investigated the temperature variation of the frequency records a value of $1332{\cdot}1$ cm.$^{-1}$ at room temperature, this diminishing slowly at first but more rapidly later to $1316{\cdot}4$ cm.$^{-1}$ at 1130° K.

The lattice dynamics developed by Raman (1943) indicates that the vibration spectrum of diamond should consist of eight frequencies of which only the first and highest representing the vibration of the two interpenetrating face-centred cubic lattices against each other, should manifest itself both as a fundamental and as an octave in the Raman Effect, whereas all the other frequencies can only appear in the second order Raman spectrum as overtones and combinations. The extensive series of investigations carried out by R. S. Krishnan (1946, 1947) and P. S. Narayanan (1951) have furnished a very complete verification of the predictions of this theory. R. S. Krishnan's investigations have also shown that, hand in hand with the change of the first order frequency shift with rise in temperature, its spectral half width also increases from $1{\cdot}7$ cm.$^{-1}$ at 300° K. to $3{\cdot}6$ cm.$^{-1}$ at 970° K.

Diamonds are known to exhibit wide variations in their optical behaviour, notably in respect of their transparency in the infra-red and ultra-violet regions of the spectrum and in the intensity and colour of the luminescence (if any) which they display. They also exhibit a great diversity in their X-ray behaviour as well, as was shown by Hariharan (1944), Krishnan (1944) and especially by G. N. Ramachandran (1944, 1946).

TABLE I

No.	Description of the specimen	Optical behaviour	Measured value of frequency in cm.$^{-1}$	Remarks
1	Irregular polycrystalline lump of bort	Translucent and feebly blue luminescent	1331·6	
2	Cube of bort with a waxy appearance	No detectable luminescence	1332·0	Faintly recorded
3	Pale yellow cube with rather rough faces		1331·9	
4	Cube appearing semi-transparent	Feebly yellow luminescent	1331·6	
5	Large coarse lump	Transparent and intensely blue luminescent	1331·8	
6	Faceted tablet, blue even in ordinary light	Transparent and brilliantly blue luminescent	1331·9	
7	Small piece cut in the form of a brilliant, pale green in ordinary light	Brilliantly green luminescent	1331·7	

8	Irregular pale yellow lump	Translucent and brilliantly orange luminescent	1331·9	
9	Semi-circular plate with a polished straight edge	Transparent, feebly blue luminescent, exhibiting 8 μ infra-red absorption and ultra-violet opaque	1331·5	Used by K. G. Ramanathan for infra-red absorption studies
10	Rectangular plate with polished edges	do.	1331·6	do.
11	Rectangular thick plate with well-polished edges	Transparent, no observable luminescence under near ultra-violet light. λ 4152 band recorded after a 24 hr. exposure	1331·8	Used by R. S. Krishnan in the work on the thermal scattering of light with λ 2536·5
12	Thick semi-circular plate with a polished straight edge	Non-luminescent and ultra-violet transparent	1331·7	Used by R. S. Krishnan to record the second order. The value recorded by him is 1331·8 cm.$^{-1}$
13	Rectangular faceted piece set in a ring	Non-luminescent	1331·7	
14	Large thick plate of irregular shape with polished edges and pale yellow in colour	do.	1331·3	Recorded with a slit width of 1·0 mm.

The studies of these authors have revealed that the faintly blue luminescent diamonds which exhibit the 8μ infra-red absorption are usually very perfect and give sharp X-ray reflections. Diamonds that are strongly blue luminescent, on the other hand, give X-ray reflections characterised by an increased integrated intensity and width which goes hand in hand with increasing intensity of luminescence. The non-luminescent diamonds which exhibit lamellar birefringence between crossed polaroids exhibited a largely increased intensity of X-ray reflection. These effects have been ascribed to a mosaicity in the structure of diamonds in the cases referred to. Though the earlier investigators have not ignored the possibility that a diversity of behaviour might also manifest itself in the Raman spectrum of diamond, it appeared desirable to reinvestigate this possibility with the aid of the extensive collection of material available at this Institute.

2. EXPERIMENTAL DETAILS

The Raman spectra were recorded with a large aperture (f 4·5) Huet two-prism glass spectrograph having a dispersion of 110 cm.$^{-1}$ per mm. in the region of λ 4630. The visible radiations of a low pressure mercury arc sufficed to excite the Raman effect. In the case of the study of luminescent diamonds a concentrated solution of sodium nitrite was interposed in the path of the exciting radiation to suppress λ 4046 line and thereby reduce considerably the continuous background due to luminescence. A slit width of 0·04 mm. was used and an exposure of one hour was found to be adequate to record the line intensely in most cases. An iron arc spectrum was superposed on the Raman spectrum and the spectrograms were measured on a Hilger photomeasuring micrometer correct to 0·001 mm. The maximum error in measurement did not exceed 0·5 cm.$^{-1}$ even in the case of lines recorded only faintly.

Any expected variation in the observed Raman spectra can manifest itself as (i) a change in the frequency shift, (ii) a variation in the width of the line and (iii) a change in the observed intensity of the line. Spurious values can arise in the measured frequency shift due to variations in the temperature of the spectrograph during the exposure. This difficulty was avoided as far as possible by giving short exposures and also by obtaining more than one spectrogram in typical cases. The Raman lines from two pairs of typical diamonds (9 & 12 and 10 & 13) were photographed simultaneously by mounting them in a line and focussing their images on the slit of the spectrograph with a large aperture lens. As the instrument used in the investigation was not of very large dispersion, it was not possible to measure the width of the line quantitatively in each case. The increase

in the width of the line due to photographic broadening has to be taken into consideration even for a qualitative finding whether there is a difference in the width of the line. The intensity of the line recorded depends on the size and shape of the specimen, its general transparency and the orientation of the plane of scattering with respect to the crystal axes. In view of the several factors entering into this question, only qualitative remarks could be made about the intensity of the line.

3. Description of the Diamonds

In all, fourteen diamonds were examined and from the description of them in Table I given above it can be seen they are representative of the diverse optical characters known to be exhibited by diamond.

4. Results and Discussion

From Table I it can be seen that the maximum difference in the measured values of the frequency shift is $0 \cdot 5$ cm.$^{-1}$ (omitting the value of No. 14, the spectrum in which case was recorded with a wide slit). The average value of the frequency shift is found to be $1331 \cdot 7$ cm.$^{-1}$, while Krishnan has reported a value of $1331 \cdot 8$ cm.$^{-1}$ using No. 12. These values fall on either side of $1331 \cdot 7$ cm.$^{-1}$ with a maximum variation of $0 \cdot 3$ cm.$^{-1}$ which is in the range of the error likely to occur in measurement.

In all the several spectra obtained, it was not possible to notice any significant variations in the width of the line after taking into account the photographic broadening in cases where the spectra were recorded intensely. It was possible to record the line in all cases with adequate intensity. Longer exposures were found to be necessary in cases where the diamonds were small, translucent or coloured. There was no observable correlation between the intensity of the Raman line and the known optical properties, *viz.*, infra-red absorption, ultra-violet transparency and the intensity and colour of the luminescence. Apparently the mosaic structure observed in diamond does not noticeably influence its Raman spectrum.

It is a pleasure to thank Prof. Sir C. V. Raman, N.L., F.R.S., for suggesting this investigation.

5. Summary

The Raman spectra of fourteen different diamonds exhibiting diverse characters in their optical behaviour (*viz.*, transparency in the infra-red and ultra-violet regions of the spectrum, birefringence and the intensity and colour of the luminescence) were recorded. The principal Raman line is found to have a frequency shift of $1331 \cdot 7 \pm 0 \cdot 2$ cm.$^{-1}$ which agrees closely

with the value of 1331·8 cm.$^{-1}$ reported earlier. There were no observable variations in the frequency shift, width or intensity of the line in the several cases studied.

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SOME ILLUSTRATIONS OF THE OPTICAL BEHAVIOUR OF IRIDESCENT CALCITE

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§1. Introduction

The structure and optical behaviour of iridescent calcite formed the subject-matter of a recent paper in these *Proceedings*.[1] The phenomena considered in that paper had their origin in the twinning layers present within the crystal; each of such layers is parallel to one edge of the rhombohedral cleavage and equally inclined to the two others. The present paper is intended as a supplement to the earlier one referred to; photographs are reproduced illustrating the various effects alluded to therein arising from reflection and refraction by the twinning layers. Amongst the phenomena illustrated may be noted particularly the following: (*a*) the formation of image patterns by multiply twinned crystals; (*b*) the vanishing of the reflections and refractions in the symmetry plane; (*c*) the appearance of sharply defined boundaries in the field of reflection and refraction; (*d*) dispersion and interference effects.

Descriptive notes on the individual figures reproduced in the Plates are given below.

§2. Descriptive Notes

Fig. 1, *Plate XIII.*—When a distant source of light is viewed through the opposing faces of a calcite rhomb traversed by more than one twinning layer, a multi-coloured pattern comprising numerous images arranged in geometric order is seen, the number and arrangement of the images being dependent on the number and disposition of the twinning layers traversed by the light. Photographs reproduced in the earlier paper illustrated cases in which three, nine, fifteen and twenty-seven images respectively were observed. In the present photograph it has been possible to record no less than thirty-six images, many of them as doublets.

Figs. 2, 3 *and* 4, *Plate XIII.*—These photographs reproduce the images of a light source observed by reflection and refraction at one twinning layer, light being incident through one face of the calcite and emerging through an adjacent face after such reflection. There are, in general, four reflected images: two in which ordinary and extraordinary waves are reflected as such and two others in which ordinary wave is transformed

to extraordinary and *vice versa*. The former are polarised in the normal manner and occur in between the latter which are polarised in the reversed fashion. The angular separation between the four species of reflections and their relative intensities vary markedly with the setting of the crystal. The positions of the images polarised in the normal manner (*i.e.*, the middle two) with respect to the two outer ones are variable. Comparing the cases reproduced as Figs. 2 and 4 it is noticed that the two have interchanged positions, while Fig. 3 illustrates the case when they are superposed.

Fig. 5, *Plate XIV*.—A linear source of white light is viewed through a calcite containing a single twinning layer held in the following manner: the twinning layer is held vertical and the source is viewed through those faces none of whose edges is parallel to the twinning layer. Three images of the slit are seen, the outer two being coloured and polarised. The deviated images are seen cut into two halves by the symmetry plane, but not so the undeviated one. The gain in intensity as we move away from the symmetry plane is clearly seen.

Figs. 6, 7 *and* 8, *Plate XIV*.—A plexiglas screen illuminated from behind by a sodium vapour lamp is viewed through the calcite rhomb held in the manner already explained above. On rotating the crystal about the vertical axis, one sees a division of the field of view into two parts differing in intensity of illumination. A dark and well-defined boundary separates the two parts of the field except where it is cut by the symmetry plane. This boundary becomes more conspicuous away from the symmetry plane in either direction. This boundary separates directions in which ordinary waves give rise to extraordinary waves from those which do not. A slight change in the above arrangement enables one to observe the boundaries at which reflections and refractions respectively of extraordinary waves as ordinary terminate. For this purpose the illuminated screen was held to one side so that the reflected or refracted light came into view and the boundary was seen as a luminous arc separating a bright from a dark field and cut into two halves by the symmetry plane. Figs. 6 and 7 show the reflection and refraction boundaries respectively. Fig. 8 demonstrates the critical transmission boundary recorded with a vertical polaroid in front of the rhomb. Observations with polarised light establish the origin of all these boundaries.

Fig. 9, *Plate XV*.—The calcite rhomb is held in the same manner as indicated for recording Fig. 5 and a linear source is viewed through it. On turning the rhomb about the vertical axis, a stage is reached when incident light grazes the twinning layer and, in addition to the refracted

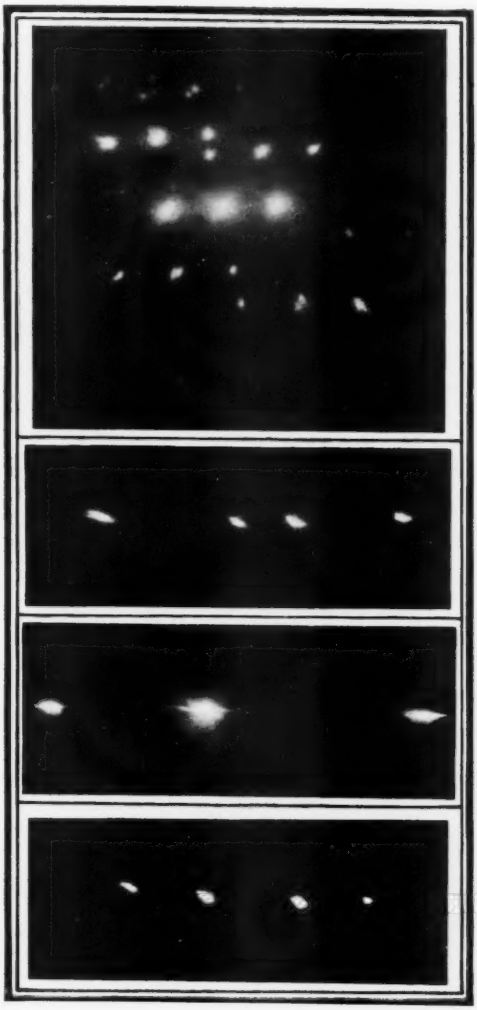

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 7

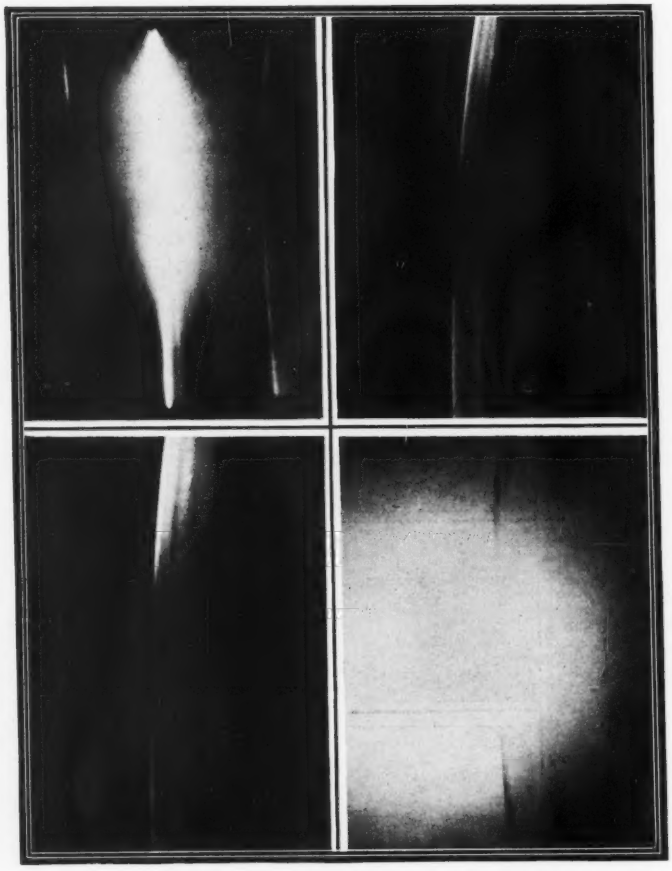

FIG. 6

FIG. 8

FIG. 9

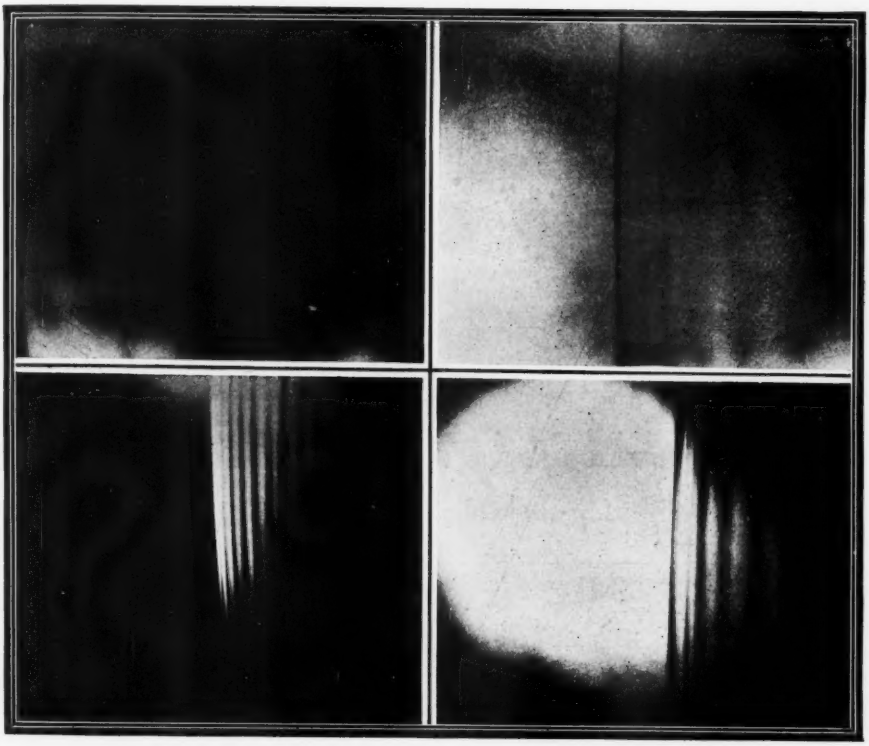

FIG. 11

FIG. 10

FIG. 12

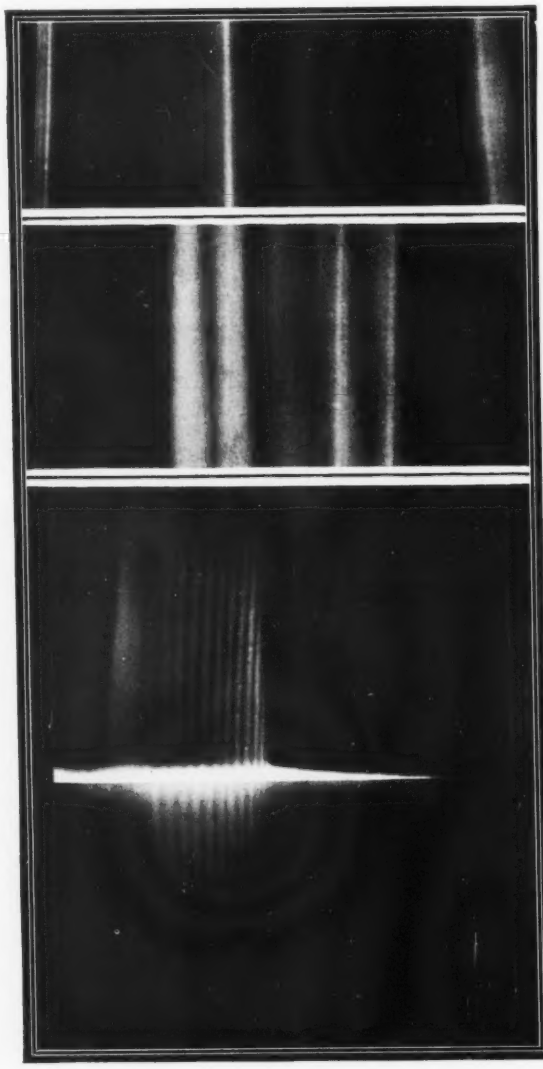

FIG. 13

FIG. 14

FIG. 15

image, a reflected one simultaneously comes into view. Polarisation studies show that extraordinary waves are reflected and refracted as ordinary to give these images. The right and left halves of Fig. 9 represent reflected and refracted images respectively, drawn out into spectra, channelled by interferences and interrupted by the symmetry plane which is horizontal. The plane of the twinning layer is vertical and separates the refracted and reflected wave-trains.

Figs. 10, 11 *and* 12, *Plate XV.*—These have been recorded in the same manner as Figs. 6, 7 and 8, but much away from the symmetry plane. Fig. 10 exhibits the interference fringes accompanying the critical reflection boundary and Figs. 11 and 12 those seen with the critical transmission boundary.

Figs. 13 *and* 14, *Plate XVI.*—These have been photographed in the following circumstances: a narrow slit backed by white light is viewed through the opposing faces of a twinned crystal. In Fig. 13, the two deviated images drawn out into spectra and channelled by two sets of interferences are seen, the central one remaining colourless. The difference in the dispersive powers for ordinary and extraordinary indices results in these dispersed spectra. The two species of interferences arise respectively from phenomena of the same nature as those exhibited by crystalline plates in polarised light and those shown by thin plates. Fig. 14 is an enlarged photograph of one of the deviated images showing dispersion and the two species of interferences.

Fig. 15, *Plate XVI.*—This was taken by arranging the illumination from an extended source of monochromatic light on the calcite rhomb in such a manner that direct transmitted light is received from above, and refracted light by oblique incidence from below. The interference fringes in the optical fields of transmission and refraction are then seen simultaneously. They are clearly seen to be complementary.

In conclusion, the author wishes to express his thanks to Professor Sir C. V. Raman for suggesting the problem and for the many helpful hints he gave me during the course of the experiments.

§3. Summary

The paper reproduces illustrations of various optical effects displayed by twinning layers in iridescent calcite. Brief descriptive notes are appended.

§4. Reference

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